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Attorney Docket No.

SP00-290

Total Pages

First Named Inventor or Application Identifier Lin He et al.

Title REDUCTION OF NITROGEN OXIDES IN DIESEL EXHAUST GASES AND INJECTION SYSTEM

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ADDRESS TO:

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1. ☒ * Fee Transmittal Form
(Submit an original and a duplicate for fee processing)
2. ☒ Specification [Total Pages 25]
(preferred arrangement set forth below)
- Descriptive title of the invention
 - Cross References to Related Applications
 - Statement Regarding Fed sponsored R&D
 - Reference to Microfiche Appendix
 - Background of the Invention
 - Brief Summary of the Invention
 - Brief Description of the Drawings (if filed)
 - Detailed Description
 - Claim(s)
 - Abstract of the Disclosure

3. ☒ Drawing(s) (35 U.S.C. § 113) [Total Sheets 1]

4. Oath or Declaration [Total Pages 2]

- a. ☒ Newly executed (original or copy)
- b. ☐ Copy from a prior application (37 C.F.R. § 1.63(d))
(for continuation/divisional with Box 16 completed)
- i. ☐ **DELETION OF INVENTOR(S)**
Signed statement attached deleting inventor(s) named in the prior application, see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).

5. ☐ Microfiche Computer Program (Appendix)
6. Nucleotide and/or Amino Acid Sequence Submission
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ACCOMPANYING APPLICATION PARTS

7. ☒ Assignment Papers (cover sheet & document(s))
8. ☒ 37 C.F.R. § 3.73(b) Statement ☐ Power of Attorney
(when there is an assignee)
9. ☐ English Translation Document (if applicable)
10. ☒ Information Disclosure Statement (IDS)/PTO-1449 ☒ Copies of IDS Citations
11. ☐ Preliminary Amendment
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(should be specifically itemized)
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☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No.: 08/

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17. CORRESPONDENCE ADDRESS

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FEE TRANSMITTAL for FY 2000

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First Named Inventor

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Examiner Name

Group / Art Unit

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SP00-290



TOTAL AMOUNT OF PAYMENT (\$1,946)

METHOD OF PAYMENT (check one)

1. ☒ The Commissioner is hereby authorized to charge indicated fees and credit any overpayments to:

Deposit Account Number **03-3325**

Deposit Account Name **Corning Incorporated**

- ☒ Charge Any Additional Fees Required Under 37 C.F.R. §§ 1.16 and 1.17

2. ☐ Payment Enclosed:

☐ Check ☐ Money Order ☐ Other

FEE CALCULATION

1. BASIC FILING FEE

Large Entity Fee Code	Fee (\$)	Fee Description	Fee Paid
101	710	Utility filing fee	
106	310	Design filing fee	
107	480	Plant filing fee	
108	690	Reissue filing fee	
114	150	Provisional filing fee	

SUBTOTAL (1) (\$ 710)

2. EXTRA CLAIM FEES

	Extra Fee from Claims below	Fee Paid
Total Claims	62 - 20** = 42 x 18 =	756
Independent Claims	9 - 3** = 6 x 80 =	480

Multiple Dependent =

**or number previously paid, if greater; For Reissues, see below

Large Entity Fee Code	Fee (\$)	Fee Description
103	18	Claims in excess of 20
102	78	Independent claims in excess of 3
104	260	Multiple dependent claim, if not paid
109	78	** Reissue independent claims over original patent
110	18	** Reissue claims in excess of 20 and over original patent

SUBTOTAL (2) (\$1,236)

FEE CALCULATION (continued)

3. ADDITIONAL FEES

Large Entity Fee Code	Fee (\$)	Fee Description	Fee Paid
105	130	Surcharge - late filing fee or oath	
127	50	Surcharge - late provisional filing fee or cover sheet	
139	130	Non-English specification	
147	2,520	For filing a request for reexamination	
112	920*	Requesting publication of SIR prior to Examiner action	
113	1,840	Requesting publication of SIR after Examiner action	
115	110	Extension for reply within first month	
116	380	Extension for reply within second month	
117	870	Extension for reply within third month	
118	1,360	Extension for reply within fourth month	
128	1,850	Extension for reply within fifth month	
119	300	Notice of Appeal	
120	300	Filing a brief in support of an appeal	
121	260	Request for oral hearing	
138	1,510	Petition to institute a public use proceeding	
140	110	Petition to revive - unavoidable	
141	1,210	Petition to revive - unintentional	
142	1,210	Utility issue fee (or reissue)	
143	430	Design issue fee	
144	580	Plant issue fee	
122	130	Petitions to the Commissioner	
123	50	Petitions related to provisional applications	
126	240	Submission of Information Disclosure Stmt	
581	40	Recording each patent assignment per property (times number of properties) ___ x	
146	690	Filing a submission after final rejection (37 C.F.R. § 1.129(a))	
149	690	For each additional invention to be examined (37 C.F.R. § 1.129(b))	

Other fee (specify) _____

Other fee (specify) _____

***Reduced by Basic Filing Fee Paid SUBTOTAL (3) (\$ 0)**

SUBMITTED BY

Completed (if applicable)

Name (Print/Type) **Anca C. Gheorghiu** Registration No. (Attorney/Agent) **44,120**

Signature *Anca Gheorghiu* Date **10.10.00**

REDUCTION OF NITROGEN OXIDES IN DIESEL EXHAUST GASES AND FUEL INJECTION SYSTEM

BACKGROUND OF THE INVENTION

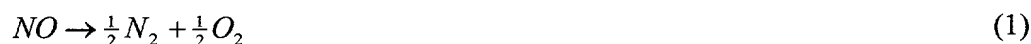
5 Nitrogen oxides (NO_x) in the earth's atmosphere are primarily emitted by automobiles and industrial plants. Studies have shown that nitrogen oxides can be hazardous to human health and the environment when present in the atmosphere in sufficiently high concentrations. For instance, nitrogen oxides above 0.05 ppm can have hazardous effects on people in good health for an exposure of over 24 hours. See,
10 Fritz, A. and Pitchon, V., "The current state of research on automotive lean NO_x catalysts," Applied Catalysis B: Environmental, Vol. 13 (1997), pp. 2. In particular, nitrogen oxides have been found to provoke lung infection and respiratory allergies. Nitrogen oxides have also been found to play an influential role in the formation of acid rain, smog, and general atmospheric visibility degradation. Because of the potential detrimental effects of nitrogen oxides on human health and the environment, the
15 government has imposed several stringent regulations on NO_x emissions. These tightened regulations continue to drive NO_x abatement technology.

Several technologies have been developed in order to decrease NO_x emissions, including passive methods using catalysts and active approaches such as
20 electrochemical catalysis, photocatalytical approaches, plasma, laser, and so forth. Rich-burning engines, such as those used in today's gasoline-powered automobiles, use a three-way catalyst to reduce NO_x emissions. The three-way catalyst typically consists of a combination of noble metals deposited on a stabilized alumina carrier. The three-way catalyst is efficient because it works together with a feedback system that directs
25 the engine to blend air and fuel in stoichiometric proportions. By controlling the air-to-fuel ratio, the engine makes hydrocarbons and carbon monoxide available in just the right amounts to reduce NO_x and unburned hydrocarbons to products like carbon dioxide, water, hydrogen gas, and nitrogen gas that are generally harmless to health and the environment. The NO_x performance of the three-way catalyst, however, rapidly
30 deteriorates in the presence of oxygen.

Removal of NO_x in lean-burn engines, *i.e.*, engines such as diesel engines that burn fuel in excess oxygen, continues to pose a great scientific challenge. There is

sufficient motivation, however, to continue to pursue a practical solution for reducing NO_x emissions in lean-burn engines because lean-burn engines provide better fuel economy than rich-burning engines. As previously mentioned, the NO_x reducing performance of the three-way catalyst, which is the standard NO_x abatement technology for gasoline engines, deteriorates rapidly in the presence of oxygen. Thus, this technology is ineffective in controlling NO_x emissions in lean exhaust gases. Some of the approaches that have been considered in controlling NO_x emissions in lean exhaust gases include catalytic decomposition of nitrogen monoxide (NO), selective catalytic reduction (SCR) with nitrogen containing compounds, and selective catalytic reduction with hydrocarbons (HC-SCR).

The decomposition of nitrogen monoxide to elements is described by the following equation:



The decomposition of nitrogen monoxide is thermodynamically favored under pressures and temperatures found in diesel exhaust. However, the decomposition reaction is inhibited by a high activation energy. Therefore, a catalyst is necessary to lower this activation energy in order to facilitate this decomposition. Various catalysts have been used to decompose NO, including precious metals, metallic oxides, and zeolites-based catalysts. One of the best catalysts recently suggested for NO decomposition is copper ion-exchanged zeolite ZSM5 (Cu/ZSM5). However, the catalytic activity of Cu/ZSM5 is greatly diminished in the presence of oxygen gas and sulfur dioxide, and the decomposition of NO is effective only at low space velocities.

In SCR with nitrogen containing compounds, a nitrogen compound, *e.g.*, ammonia or urea, is used as a reducing agent for nitrogen oxides to produce innocuous products. In reactions (2) and (3) below, ammonia is used as the reducing agent for nitrogen oxides to produce nitrogen and water:



The reactions (2) and (3) are favored in the presence of oxygen. In the presence of oxygen, a catalyst such as vanadium pentoxide (V_2O_5) supported on oxides such as TiO_2 , Al_2O_3 , and SiO_2 is used to facilitate the reaction. In NH_3 -SCR, an external source of ammonia is needed to reduce NO_x to N_2 . NH_3 -SCR is widely used as a pollution reduction technique in stationary plants such as electric power plants. The toxicity and handling problems associated with ammonia, however, has limited the use of the technology in motor vehicles.

U.S. Patent 5,863,508 issued to Lachman *et al.* describes a multi-stage catalytic reactor system which allows ammonia to be synthesized onboard a vehicle and then used to reduce NO_x to N_2 as previously described in reactions (2) and (3) above. The reactor system includes two units, each of which includes multiple open-ended cells. A portion of the cells in the first unit include a first stage catalyst, which is a noble metal on a support. The noble metal cannot be rhodium. Exhaust gases from combustion are passed through the first unit so that a portion of the NO_x in the exhaust gases is reduced to ammonia by the first stage catalyst. The modified exhaust gas mixture is then passed to the second unit, wherein the ammonia in the modified gas mixture is reacted with the remaining NO_x to yield a converted gas mixture. An external source of ammonia is not needed because the ammonia is generated in the first unit. The passage of the exhaust gases through the first and second units results in conversion of NO_x , CO, and hydrocarbons to innocuous products. This technology is effective for lean burn engines.

HC-SCR was discovered during the survey of the effect of co-existing gases on the catalytic activity of Cu/ZSM5. In HC-SCR, hydrocarbons, *e.g.*, ethane, propane, and propene, selectively react with NO_x to produce nitrogen, carbon dioxide, and water:



There are three principal types of catalysts active for the HC-SCR, including zeolites, oxide-type catalysts, and supported noble metals. See, for example, Iwamoto, M. and Mizuno, N., "NO_x emission control in oxygen-rich exhaust through selective catalytic reduction by hydrocarbon," *Journal of Automobile Engineering* (1993), pp. 23-33, and Fritz, A. and Pitchon, V., "The current state of research on automotive lean NO_x catalysts," *supra*, pp. 10-25, for additional discussions on catalysts for HC-SCR. In this

technology, additional HC must be supplied and a system is required to deliver the HC. Controlling the amount of HC needed is a great challenge. Furthermore, excess oxygen may affect NO_x conversion.

SUMMARY OF THE INVENTION

5 In one aspect, the invention relates to a method for reducing NO_x in lean exhaust gases to N₂. The method comprises injecting a fuel into the exhaust gases and passing the exhaust gases and fuel mixture through a catalyst to reduce the NO_x to N₂.

10 In another aspect, the invention relates to a fuel injection system which comprises a catalytic reactor having an inlet end that receives exhaust gases and an outlet end that outputs converted exhaust gases. The fuel injection system further includes a catalyzed substrate mounted inside the catalytic reactor for reducing NO_x in the received exhaust gases to N₂ in the presence of a fuel. The fuel injection system further includes a fuel injector for injecting the fuel upstream of the catalyzed substrate.

15 In another aspect, the invention relates to a catalyst composition for reducing NO_x in lean exhaust gases to N₂ using a fuel as the reductant. In some embodiments, the catalyst composition comprises a perovskite compound represented by the formula AB_{1-x}PM_xO₃, where A is a rare-earth metal, B is a transition metal, PM is a precious metal, and O is oxygen. In some embodiments, the catalyst composition comprises at least one metal oxide impregnated with at least one precious metal. In some
20 embodiments, the catalyst composition comprises a zeolite impregnated with at least one precious metal. In some embodiments, the catalyst composition comprises a combination of a zeolite and at least one metal oxide impregnated with at least one precious metal.

25 In another aspect, the invention relates to a catalytic unit for reducing NO_x in lean exhaust gases to N₂ using a fuel as the reductant. In some embodiments, the catalytic unit comprises a body extruded from a zeolite which is impregnated with at least one precious metal. In some embodiments, the catalytic unit comprises a ceramic substrate coated with a catalytic material. In some embodiments, the catalytic material includes at least one metal oxide impregnated with at least one precious metal. In some
30 embodiments, the catalytic material includes a combination of a zeolite and at least one metal oxide impregnated with at least one precious metal. In some embodiments, the

catalytic includes a perovskite compound represented by the formula $AB_{1-x}PM_xO_3$, where A is a rare-earth metal, B is a transition metal, PM is a precious metal, and O is oxygen.

Other aspects and advantages of the invention will be apparent from the following description and the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 schematically shows a reductant injection system in accordance with an embodiment of the invention.

Figure 2 shows a setup for evaluating the deNO_x catalysts of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Embodiments of the invention provide a NO_x de-pollution (deNO_x) catalyst and a reductant injection system which uses the deNO_x catalyst. In the reductant injection system, diesel fuel is post-injected into diesel exhaust gas and used as a reductant for the reduction of NO_x to N₂ through the deNO_x catalyst. Diesel fuel is injected continuously or periodically based on the requirement of the total NO_x conversion and fuel penalty. In some embodiments of the invention, the deNO_x catalyst includes one or more perovskite compounds represented by the formula $AB_{1-x}PM_xO_3$, where A is a group III or group IV rare-earth metal, B is a group III or group IV transition metal, PM is a precious metal, O is oxygen. Preferably, x ranges from 0.01 to 0.3. In some embodiments of the invention, the deNO_x catalyst includes a support material impregnated with a precious metal or a combination of precious metals. The support material is made of a metal oxide or a combination of two or more metal oxides. In some embodiments of the invention, the deNO_x catalyst includes a zeolite impregnated with a precious metal, or a combination of precious metals. Zeolites are silicates consisting of interlocking tetrahedrons of SiO_x and AlO_y. In some embodiments, of the invention, the deNO_x catalyst includes a combination of a zeolite and metal oxide impregnated with a precious metal, or a combination of precious metals.

Various embodiments of the invention will now be described with reference to the accompanying figures. Figure 1 schematically shows a reductant injection system

which includes a catalytic reactor 4 having an inlet end 6 for receiving exhaust gases 8 and an outlet end 10 for outputting converted exhaust gases 12. A deNO_x catalyst 14 is mounted inside the catalytic reactor 4. A port 16 is provided in the wall of the catalytic reactor 4, upstream of the deNO_x catalyst 14. The reductant injection system 2 further comprises a fuel injector 18 which is coupled to the port 16. Preferably, the fuel injector 18 is as close as possible to the deNO_x catalyst 14. In operation, exhaust gases 8 are introduced into the catalytic reactor 4 through the inlet end 6. Diesel fuel 20 is injected into the catalytic reactor 4 through the port 16. The diesel fuel 20 may be injected continuously or periodically. The injected diesel fuel 20 mixes with the exhaust gases 8. The resulting mixture then passes through the deNO_x catalyst 14. The deNO_x catalyst 14 converts NO_x into innocuous products. The converted gas mixture 12 exits the catalytic reactor 4 through the outlet end 10.

Catalytic activities of various embodiments of the deNO_x catalyst 14 are evaluated by placing individual deNO_x catalysts inside the catalytic reactor 4 and passing exhaust gases mixed with diesel fuel through the catalysts. For the reduction of NO_x to N₂ using diesel fuel, simulated diesel exhaust gases having the composition indicated in Table 1 are introduced into the inlet end 6 of the catalytic reactor 4.

Table 1: Composition of Simulated Diesel Exhaust Gases

Gas	Amount (by volume)
O ₂	3-6 percent
CO ₂	14 percent
NO _x	500-1065 ppm
CO	350 ppm
H ₂ O	10-12 percent

The conversion of NO_x to N₂ is studied by varying the amount of diesel fuel injected through the port 16 into the catalytic reactor 2. In the study, the diesel fuel is injected by a gasoline fuel injector, which, for safety reasons, had a lower pressure in comparison with a typical diesel fuel injector. This lower injection pressure may result

in incomplete fuel consumption. The typical fuel injection rates in the study are 2.2 mg/s, 1.75 mg/s, and 1.4 mg/s of diesel fuel, which correspond to 0.004, 0.0035, and 0.003 injection cycles, respectively. In a period of t seconds, u injection cycle means that the fuel is injected for $t \cdot u$ seconds. For a 1000-second period, for example, 0.004 injection cycle means that the fuel is injected for 4 seconds.

For comparison purposes, catalyst activity using synthetic hydrocarbons as the exhaust gases is also investigated. For the reduction of NO_x to N_2 using synthetic hydrocarbons, synthetic gas mixture having the composition indicated in Table 2 is introduced into the inlet end 6 of the catalytic reactor 4.

Table 2: Composition of Synthetic Gas Mixture

Gas	Amount (by volume)
O_2	0.77 percent
CO_2	14 percent
NO_x	1000 ppm
CO	1000 ppm
C_3H_6	333 ppm
C_3H_8	167 ppm
H_2	0.33 percent
H_2O	10-12 percent

The synthetic gas mixture in Table 2 gives approximately 1.2 redox ratio. The synthetic gas flow is nitrogen-balanced, resulting in a total flow of 7508 ml/min. This flow rate corresponds to a space velocity of 35,000 per hour. The space velocity can be varied by adjusting the feed flow rates of the gas mixture. Typically, the catalytic activity is measured with the catalytic reactor 2 operating within a temperature range of 60 °C to 600 °C. A temperature ramp rate is set for 8.5 °C/min until the catalytic reactor 2 reaches 600 °C, and then the operating temperature of the catalytic reactor 2 is maintained at this temperature for approximately 15 minutes.

Prior to each run, the gases introduced into the inlet end 6 of the catalytic reactor 2 are quantified. A mass balance of the initial NO_x concentration in the inlet gas mixture with respect to the amount of NH₃, N₂O, and NO₂ formed downstream of the catalyzed substrate is used to determine the amount of N₂ produced. The percent total NO conversion and the percent amount of NH₃ and N₂ formed are determined by the following equations:

$$\text{Total NO conversion(\%)} = \left[\left(\frac{C_{NO}}{C_{NO,in}} \right) - 1 \right] \times 100 \quad (5)$$

$$\text{NH}_3(\%) = \frac{C_{NH_3}}{C_{NO,in}} \times 100 \quad (6)$$

$$\text{N}_2(\%) = \text{NO conversion(\%)} - [\text{NH}_3(\%) + \text{NO}_2(\%) + 2 \times \text{N}_2\text{O}(\%)] \quad (7)$$

As shown in Figure 2, the converted gas mixture 12 downstream of the deNO_x catalyst 14 is analyzed by a Fourier Transform Infrared Spectrometer (FTIR) 22, such as one sold under the trade name Magna Infrared 560 Spectrometer by Nicolet Instrument Corporation, Madison, WI. FTIR 22 allows all the species of interest such as NO, NH₃, N₂O, NO₂, CO, CO₂, H₂O, C₃H₆, C₃H₈, and other hydrocarbons to be simultaneously monitored.

The following examples of deNO_x catalysts are subjected to the testing procedure to determine their effectiveness in converting NO_x to innocuous products using the reductant injection system 2 described above. It should be clear that the following examples are intended for illustration purposes and are not intended to limit the scope of the invention as otherwise described herein.

EXAMPLE 1

In one embodiment of the invention, the deNO_x catalyst 14 (shown in Figure 1) includes one or more perovskite compounds represented by the formula AB_{1-x}PM_xO₃, where A is a group III or group IV rare-earth metal, B is a group III or group IV transition metal, PM is a precious metal, O is oxygen. Preferably, x ranges from 0.01

to 0.3. To obtain a relatively high surface area, the perovskite-based deNO_x catalyst can be synthesized by a method called the Pechini process. For a C1 deNO_x catalyst based on a perovskite compound LaMn_{0.9}Ru_{0.1}O₃, the Pechini process involves dissolving lanthanum nitrate in aqueous manganese nitrate and adding citric acid and ethylene glycol to the mixture to obtain a chelated complex. The ratio of citric acid to lanthanum (La) and manganese (Mn) is one to one, *e.g.*, two moles of citric acid to one mole of LaMn_{0.9}Ru_{0.1}O₃. The amount of ethylene glycol to add to the mixture is calculated by the following equation:

$$\text{weight of ethylene glycol} = 1.5 \times \text{weight of citric acid} \times \frac{1}{\text{density of ethylene glycol}} \quad (8)$$

The chelated complex is heated to 90 °C to form a gel. The temperature of the gel is then increased to 120 °C to remove all the water and NO_x fumes, and the gel is puffed out, *i.e.*, ignited, to get the powder. The puffed-out powder is fired at 450 °C for 4 hours to dry and remove carbon from the powder. After that, the powder is sintered at 700 °C or any desirable temperature to get the final product. The powder is ball milled for 2-5 days. About 90 percent of the milled powder is then combined with about 10 percent of a binder, *e.g.*, colloidal alumina sold under the trade name Al-20 by PQ corporation, Philadelphia, PA, to form a washcoat slurry. A ceramic substrate, *e.g.*, cordierite honeycombs made by Corning, Inc., Corning, New York, under the trade name Celcor®, is dipped in the washcoat slurry. In general, any ceramic substrate that can withstand temperatures of about 150 °C to 600 °C can be used in the invention. The ceramic substrate is fired in air or reducing atmosphere, *e.g.*, forming gas or nitrogen gas, or exhaust gas at 600 °C for 3 hours with a ramp rate of 3 °C/min.

The composition of the C1 deNO_x catalyst is as follows: 90 percent LaMn_{0.9}Ru_{0.1}O₃ and 10 percent Al₂O₃. Activity of this catalyst in simulated diesel exhaust gases (see Table 1) was evaluated using the testing procedure outlined above (see Figure 2). As shown in Table 3, the C1 deNO_x catalyst demonstrated a high total NO conversion of 81.5 to 96.3 percent with diesel fuel injection rate of 1.4 mg/s and outlet temperature of 300 °C to 500 °C, *i.e.*, temperature at the outlet end 10 of the catalytic reactor 2 (shown in Figure 1). About 70 to 84 percent of N₂ is generated in the outlet temperature window with 10 to 12 percent NH₃ as a by-product. The

concentrations of N_2O and NO_2 are negligible. The high NO conversion indicates that C1 can crack the diesel fuel efficiently to lighter hydrocarbon or reducing agents which can enhance the reduction of NO_x to N_2 . Decreasing the amount of the diesel fuel injected upstream of the catalyst can reduce the amount of NH_3 produced.

5 Table 3: Summary of Catalyst Activity for C1 De NO_x Catalyst Using Simulated Diesel Exhaust Gases

O_2 (%)	Diesel Injection Rate (mg/s)	Outlet Temp. ($^{\circ}C$)	Total NO Conversion (%)	NH_3 (%)	N_2 (%)	Initial NO (ppm)
6	1.4	300	88.5	11.5	77	480
6	1.4	350	92.3	10.4	81.9	480
6	1.4	380	95.9	12.5	83.4	480
6	1.4	404	96.3	11.7	84.6	480
6	1.4	430	95.4	11.0	84.4	480
6	1.4	483	79.4	10.4	69	480
6	1.4	520	81.5	11.5	70	480

10 For comparison purposes, the catalytic performance of the C1 de NO_x catalyst was also tested in a synthetic gas mixture (see Table 2). In this case, the synthetic gases were used as reductants. As shown in Table 4, the highest NO to N_2 conversion observed is 33.5 percent at outlet temperature of 576 $^{\circ}C$. At lower temperatures such as 300 $^{\circ}C$, NO conversion was as low as 4 percent. As can be observed from the data in Tables 3 and 4, the NO to N_2 conversion is much lower when synthetic gases were used instead of diesel fuel.

Table 4: Summary of Catalyst Activity for C1 DeNO_x Catalyst Using Synthetic Gas Mixture

O ₂ (%)	Diesel Injection Rate (mg/s)	Outlet Temp. (°C)	Total NO Conversion (%)	NH ₃ (%)	N ₂ (%)	Initial NO (ppm)
6	0	300	4	0	4	1080
6	0	400	12	0	12	1080
6	0	500	25.5	0	25.5	1080
6	0	576	33.5	0	33.5	1080

EXAMPLE 2

In another embodiment of the invention, the deNO_x catalyst 14 includes a support material impregnated with one or more precious metals. Examples of precious metals suitable for use in the invention are rhodium (Rh), platinum (Pt), palladium (Pd), iridium (Ir), and ruthenium (Ru). The support material is made of a metal oxide or a combination of two or more metal oxides. A C2 deNO_x catalyst is attained by impregnation of non-stoichiometric titanium oxide (TiO_{2-x}) with Rh and Pt. In this example, x is 0.25. The non-stoichiometric titanium oxide is obtained by mixing one mole of Ti₂O₃ and two moles of TiO₂ and then firing the mixture at 1100 °C for 5 hours in forming gas (6 percent H₂/94 percent N₂). The fired mixture is impregnated with Pt by dipping repeatedly in (NH₃)₄Pt(NO₃)₂ solution. The resulting mixture is dried in an oven at 110 °C to 120 °C for 24 hours and then fired for three hours in air at 560°C. The Pt-TiO_{2-x} mixture is impregnated with Rh by dipping repeatedly in Rh solution. The resulting mixture is dried in an oven at 110 °C to 120 °C for 24 hours and then fired for three hours in air at 560°C to obtain Rh-Pt/TiO_{2-x}.

The fired mixture Rh-Pt/TiO_{2-x} is milled for 2-5 days. Then about 90 percent of the milled powder is combined with about 10 percent of a binder, *e.g.*, colloidal alumina, to form a washcoat slurry. A ceramic substrate, *e.g.*, cordierite honeycombs sold by Corning, Inc., Corning, NY, under the trade name Celcor®, is dipped or

washcoated in the slurry. In general, any ceramic substrate that can withstand temperatures of approximately 150 °C to 600 °C can be used in the invention. A washcoat loading in the range of 30 to 40 percent is observed on the honeycomb substrate. The washcoated substrate is then fired in air or reducing atmosphere, *e.g.*, forming gas or nitrogen gas, or exhaust gas at 600 °C for 3 hours with ramp rate of 3 °C/min. The composition of the C2 deNO_x catalyst is as follows: 1 percent by weight Rh, 2 percent by weight Pt, 90 percent by weight TiO_{2-x}, and 10 percent by weight Al₂O₃ (binder). Typically, the amount of Rh will be in a range from 0.01 to 5 percent, the amount of Pt will be in a range from 0.01 to 5 percent, and the amount of TiO_{2-x} will be in a range from 0 to 100%.

Activity of the C2 deNO_x catalyst in simulated diesel exhaust gases (see Table 1) was evaluated using the testing procedure described above (see Figure 2). As shown in Table 5, the C2 deNO_x catalyst demonstrated a high total NO conversion of 73 to 81.6 percent with diesel fuel injection rate of 1.75 mg/s and catalytic reactor outlet temperature of 450 °C to 560 °C. For a diesel injection rate of 2.2 mg/s and catalytic reactor outlet temperature of 445 °C to 562 °C, the C2 deNO_x catalyst demonstrated a very high total NO conversion of 91.8 to 96.4 percent. This shows that increasing the fuel injection amount results in higher N₂ generation. However, the undesirable NH₃ generation also increases as the fuel injection amount is increased (see Table 5). For the C2 deNO_x catalyst, the optimized condition is that the injection amount is less than 1.75 mg/s.

Table 5: Summary of Catalyst Activity for C2 DeNO_x Catalyst Using Simulated Diesel Exhaust Gases

O ₂ (%)	Diesel Injection Rate (mg/s)	Outlet Temp. (°C)	Total NO Conversion (%)	NH ₃ (%)	N ₂ (%)	Initial NO (ppm)
6	1.75	450	73	4	69	511
6	1.75	480	77.1	4.1	73	511
6	1.75	520	81.6	6.1	75.5	511
6	1.75	560	76.7	6.8	70	511
6	2.2	445	91.8	11.2	80.6	501
6	2.2	490	96.4	11.6	84.8	501
6	2.2	518	94.6	12.6	82	501
6	2.2	562	93	10.4	82.6	501

EXAMPLE 3

In another embodiment of the invention, the deNO_x catalyst **14** (shown in Figure 1) includes a zeolite impregnated with one or more precious metals. Examples of precious metals suitable for use in the invention are Pt, Rh, Ru, Pd, and Ir. As previously mentioned, zeolites are silicates consisting of interlocking tetrahedrons of SiO_x and AlO_y. An example of a zeolite that is suitable for use in the invention is ZSM-5. For high temperature stability, the silica to alumina mole ratio in the zeolite should be high. For example, for ZSM-5, the silica to alumina mole ratios is at least about 25, and preferably at least about 55. One source of ZSM-5 zeolite is supplied by Exxon Mobil Corp., Dallas, TX, under the trade name MZ-12. Other examples of zeolites evaluated for use in the invention include mesoporous crystalline material (MCM-41), ultrastabilized Y (USY), NaY, H-ferrierite, and AlPO₄-5. In some embodiments of the invention, the zeolites are loaded with transition metals, *e.g.*, Cu, In, Ga, Ni, Ag, or Co, or combinations thereof. H-ferrierite loaded with Ni-Co or Ag

has been shown to be effective in reducing NO₂ to N₂. The catalyst may include up to 5 percent precious metals and up to 5 percent transition metals.

A C3 deNO_x catalyst is attained by impregnation of Ni-Co loaded MZ-12 (ZSM-5; Si/Al=55) zeolite with Pt. MZ-12 zeolite is loaded with 1.5 percent Ni and 1.5 percent Co. The metals, Ni and Co, are added as their nitrate precursors. The MZ-12 zeolite is first weighed out, and amounts of nickel nitrate and cobalt nitrate to be combined with the zeolite are calculated. The nitrates are then dissolved in deionized water. MZ-12 zeolite powder is dispersed in the solution. The mixture is then stirred well followed by drying in an oven at about 110 °C to 120 °C for about 24 hours. The resulting dried powder is calcined at a ramp rate of 3 °C/min to about 600 °C and held at that temperature for about 3 hours in air to obtain Ni-Co/MZ-12. The calcined mixture is extruded into honeycombs. Prior to extrusion, specific amounts of methocel, silicon resin, dibenzyl ether, and oleic acid are added to the calcined mixture. Both 200 and 400 cell density per square inch (cps) were extruded and fired at 850 °C for 3 hours. The extruded honeycomb bodies were impregnated with 2 percent Pt by dipping repeatedly in a 2 percent (NH₃)₄Pt(NO₃)₂ solution. Prior to catalytic testing, the samples are fired under air for 3 hours at 600 °C.

The composition of the C3 deNO_x catalyst is as follows: 2 percent Pt, 1.5 percent Ni, 1.5 percent Co, 90 percent MZ-12, and 10 percent Al₂O₃. Activity of this catalyst in simulated diesel exhaust gases (see Table 1) was evaluated using the testing procedure outlined above. As shown in Table 6, the C3 deNO_x catalyst demonstrated a high total NO conversion of 71 to 77 percent with diesel fuel injection rate of 1.4 mg/s and catalytic reactor outlet temperature of 446 °C to 505 °C. For a diesel injection rate of 2.2 mg/s and catalytic reactor outlet temperature of 550 °C to 600 °C, the C3 deNO_x catalyst demonstrated a high total NO conversion of 86 percent.

Table 6: Summary of Catalyst Activity for C3 DeNO_x Catalyst Using Simulated Diesel Exhaust Gases

O ₂ (%)	Diesel Injection Rate (mg/s)	Outlet Temp. (°C)	Total NO Conversion (%)	NH ₃ (%)	N ₂ (%)	Initial NO (ppm)
3	1.4	446	71.2	7	64.2	1065
3	1.4	505	77	7.5	69.5	1065
6	2.2	550-600	86.1	9	77.1	524

EXAMPLE 4

In another embodiment of the invention, the deNO_x catalyst 14 (shown in Figure 1) includes a zeolite and metal-oxide mixture impregnated with one or more precious metals. A C4 deNO_x catalyst is attained by impregnation of 50 percent MZ-12 (ZSM-5; Si/Al=55) zeolite and alumina mixture with a 1.12 g iridium (Ir) solution made from IrCl₃·3H₂O to achieve a 45 g/ft³ washcoat loading on a 3.25 in. x 1 in. ceramic substrate, *e.g.*, cordierite honeycombs made by Corning, Inc., Corning, NY, under the trade name Celcor®, with a cell density of 400 cpsi. The alumina in the zeolite and alumina mixture may exist in its various forms including La-γ-β-Al₂O₃. The C4 catalyst is prepared using a method similar to the one described for the C2 catalyst. The alumina binder used in this example is 15 percent colloidal alumina, *e.g.*, colloidal alumina under the trade name Al-20 by PQ corporation. All catalytically tested substrates have a diameter of about 1 inch and a length of about 1 inch. In an alternative embodiment, the C4 deNO_x catalyst may be formed by drying the zeolite, alumina, and iridium mixture in an oven and then firing the dried mixture. The fired mixture may be extruded into honeycombs.

The composition of the C4 deNO_x catalyst is as follows: 1 percent Ir, 50 percent ZSM-5 zeolite, such as one sold under the trade name MZ-12 by Exxon Mobil, Corp., Dallas, TX, and 50 percent Al₂O₃. Activity of this catalyst in simulated diesel exhaust gases (see Table 1) was evaluated using the testing procedure outlined above. The

catalytic activity was evaluated under various oxygen concentrations (3 to 5 percent) with constant fuel injection rate of 1.4 mg/s. As shown in Table 7, the C4 deNO_x catalyst demonstrated a high total NO conversion of 70 to 96 percent with diesel fuel injection rate of 1.4 mg/s and catalytic reactor outlet temperature of 390 °C to 516 °C. Maximum N₂ generations of 93 percent, 90.7 percent, and 83.4 percent were observed at 400 °C with 3 percent, 4 percent, and 5 percent oxygen, respectively. The N₂ generation decreased with increasing temperature. The undesirable by-product NH₃ was relatively low. The total NO_x conversion using catalyst C4 were very high when the simulated diesel exhaust gases contained 3 percent and 4 percent oxygen.

Table 7: Summary of Catalyst Activity for C4 DeNO_x Catalyst Using Simulated Diesel Exhaust Gases

O ₂ (%)	Diesel Injection Rate (mg/s)	Outlet Temp. (°C)	Total NO Conversion (%)	NH ₃ (%)	N ₂ (%)	Initial NO (ppm)
3	1.4	400	96	3	93	525
3	1.4	419	96.6	11.6	85	525
4	1.4	390	94.1	3.4	90.7	525
4	1.4	431	95.4	6.3	89.1	525
5	1.4	393	87.4	4	83.4	525
5	1.4	438	62.7	3	59.7	525
5	1.4	516	70.5	4.6	65.9	525

The deNO_x catalysts of the invention demonstrate high activities for the reduction of NO_x to N₂ in simulated diesel exhaust gases using diesel fuel as reductant. No other fuel or gas tanks are needed to be installed because on-board diesel fuel can be used. The amounts of NO₂ and N₂O generation are minimal. The catalyst may be extruded, resulting in a material with a larger volume of catalyst than in the washcoated case, which may lead to enhanced performance. It is observed by FTIR (22 in Figure 2) that a lot of light hydrocarbons are not used, which means that fuel penalty can be decreased. A partial oxidation catalyst (not shown) may be added downstream of the

deNO_x catalysts (14 in Figure 1). Adding a partial oxidation catalyst downstream of the deNO_x catalysts can (a) decrease the emission of the hydrocarbon into atmosphere, (b) use the hydrocarbon generated by diesel fuel partial oxidation to reduce NO to N₂, (subsequently, NO is also reduced by acting as an oxidant for the hydrocarbon) and (c) decrease the requirement of the NO conversion at the deNO_x catalyst, *i.e.*, the amount of the fuel injected will be decreased.

To enhance total NO_x reduction, some metal or metal oxides are active for partially cracking diesel into lighter and efficient reductants. Such metal or metal oxides may include the following: precious metal, transition metal/metal oxide, and rare earth metal/metal oxide or their combination. A considerable advantage in activity is expected to be gained from a high pressure diesel injector, which will atomize the fuel. Perovskite compound has low surface area. Its catalytic performance can be enhanced by increasing surface area with different synthesizing methods, *e.g.*, the Pechini process described above. Gasoline is an alternative reductant that may be used instead of diesel to reduce charring. Gasoline is expected to lower the light off temperature for NO_x reduction.

While the invention has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope of the invention as disclosed herein. Accordingly, the scope of the invention should be limited only by the attached claims.

CLAIMS

What is claimed is:

1. A method for reducing NO_x in lean exhaust gases to N_2 , the method comprising:
5 injecting a fuel into the exhaust gases; and
passing the exhaust gases and fuel mixture through a catalyst to reduce the NO_x
in the exhaust gases to N_2 .
2. The method of claim 1, further comprising passing the NO_x reduced exhaust
10 gases through a partial oxidation catalyst.
3. The method of claim 1, wherein the fuel is selected from the group consisting of
diesel fuel and gasoline.
4. The method of claim 1, wherein the catalyst comprises a perovskite compound
15 represented by the formula $\text{AB}_{1-x}\text{PM}_x\text{O}_3$, where A is a rare-earth metal, B is a transition
metal, PM is a precious metal, and O is oxygen.
5. The method claim 4, wherein A comprises lanthanum, B comprises manganese,
20 PM comprises ruthenium, and x ranges from about 0.01 to 0.3.
6. The method of claim 1, wherein the catalyst comprises at least one metal oxide
impregnated with at least one precious metal.
7. The method of claim 6, wherein the metal oxide comprises one selected from
25 the group consisting of TiO_{2-x} and Al_2O_3 .
8. The method of claim 7, wherein x is 0.25.
9. The method of claim 6, wherein the precious metal is selected from the group
30 consisting of Pt, Pd, Rh, Ru, Ir, and combinations thereof.

10. The method of claim 1, wherein the catalyst comprises a zeolite impregnated with at least one precious metal.

11. The method of claim 10, wherein the zeolite comprises one selected from the group consisting of MCM-41, ultrastabilized Y, NaY, H-ferrierite, $\text{AlPO}_4\text{-5}$, and ZSM-5.

12. The method of claim 8, wherein the zeolite is loaded with a metal selected from the group consisting of Cu, Ni, In, Ga, Ag, Co, and combinations thereof.

13. The method of claim 1, wherein the catalyst comprises a combination of a zeolite and at least one metal oxide impregnated with at least one precious metal.

14. The method of claim 13, wherein the metal oxide comprises Al_2O_3 .

15. The method of claim 13, wherein the precious metal comprises one selected from the group consisting of Pt, Pd, Rh, Ru, Ir, and combinations thereof.

16. The method of claim 13, wherein the zeolite comprises one selected from the group consisting of MCM-41, ultrastabilized Y, NaY, H-ferrierite, $\text{AlPO}_4\text{-5}$, and ZSM-5.

~~17.~~ An exhaust gas NO_x reducing system, comprising:
a catalytic reactor having an inlet end which receives the exhaust gases and an outlet end which outputs converted exhaust gases;
a catalyzed substrate mounted inside the catalytic reactor for reducing NO_x in the received exhaust gases to N_2 in the presence of a fuel; and
a fuel injector for injecting the fuel upstream of the catalyzed substrate.

18. The system of claim 17, further comprising a partial oxidation catalyst mounted downstream of the catalyzed substrate.

19. The system of claim 17, wherein the fuel comprises one selected from a group consisting of diesel fuel and gasoline.

20. The system of claim 17, wherein the catalyst comprises a perovskite compound represented by the formula $AB_{1-x}PM_xO_3$, where A is a rare-earth metal, B is a transition metal, PM is a precious metal, and O is oxygen.

21. The system of claim 20, wherein A comprises lanthanum, B comprises manganese, PM comprises ruthenium, and x ranges from about 0.01 to 0.3.

22. The system of claim 17, wherein the catalyst comprises at least one metal oxide impregnated with at least one precious metal.

23. The system of claim 22, wherein the metal oxide comprises TiO_{2-x} .

24. The system of claim 22, wherein the precious metal comprises one selected from the group consisting of Pt, Pd, Rh, Ru, Ir, and combinations thereof.

25. The system of claim 17, wherein the catalyst comprises a zeolite impregnated with at least one precious metal.

26. The system of claim 25, wherein the zeolite comprises one selected from the group consisting of MCM-41, ultrastabilized Y, NaY, H-ferrierite, $AlPO_4-5$, and ZSM-5.

27. The system of claim 25, wherein the zeolite is loaded with a metal selected from the group consisting of Cu, Ni, In, Ga, Ag, Co, and combinations thereof.

28. The system of claim 25, wherein the precious metal comprises one selected from the group consisting of Pt, Pd, Rh, Ru, Ir, and combinations thereof.

29. The system of claim 17, wherein the catalyst comprises a combination of a zeolite and at least one metal oxide impregnated with at least one precious metal.

30. The system of claim 29, wherein the zeolite comprises one selected from the group consisting of MCM-41, ultrastabilized Y, NaY, H-ferrierite, $\text{AlPO}_4\text{-5}$, and ZSM-5.

31. The system of claim 29, wherein the precious metal comprises one selected from the group consisting of Pt, Pd, Rh, Ru, Ir, and combinations thereof.

32. The system of claim 29, wherein the metal oxide comprises Al_2O_3 .

33. A catalyst composition for reducing NO_x in lean exhaust gases to N_2 using a fuel as a reductant, comprising a perovskite compound represented by the formula $\text{AB}_{1-x}\text{PM}_x\text{O}_3$, where A is a rare-earth metal, B is a transition metal, PM is a precious metal, and O is oxygen.

34. The catalyst composition of claim 33, wherein x ranges from about 0.01 to 0.3.

35. The catalyst composition of claim 33, wherein A comprises lanthanum.

36. The catalyst composition of claim 33, wherein B comprises manganese.

37. The catalyst composition of claim 33, wherein PM comprises platinum.

38. The catalyst composition of claim 33, wherein A comprises lanthanum, B comprises manganese, PM comprises platinum, and x ranges from about 0.01 to 0.3.

39. A catalyst composition for reducing NO_x in lean exhaust gases to N_2 using a fuel as the reductant, comprising at least one metal oxide impregnated with at least one precious metal.

40. The catalyst composition of claim 39, wherein the metal oxide comprises TiO_{2-x} .

41. The catalyst composition of claim 39, wherein the precious metal comprises one selected from the group consisting of Rh, Pt, Pd, Ir, Ru, and combinations thereof.

42. A catalyst composition for reducing NO_x in lean exhaust gases to N_2 using a fuel as a reductant, comprising a zeolite impregnated with at least one precious metal.

43. The catalyst composition of claim 42, wherein the zeolite comprises one selected from the group consisting of MCM-41, ultrastabilized Y, NaY, $\text{AlPO}_4\text{-5}$, H-ferrierite, and ZSM-5.

44. The catalyst composition of claim 42, wherein the zeolite is loaded with a metal selected from the group consisting of Cu, Ni, In, Ga, Ag, Co, and combinations thereof.

45. The catalyst composition of claim 42, wherein the precious metal comprises one selected from the group consisting of Pt, Pd, Rh, Ru, Ir, and combinations thereof.

46. A catalyst composition for reducing NO_x in lean exhaust gases to N_2 using a fuel as a reductant, comprising a combination of a zeolite and at least one metal oxide impregnated with at least one precious metal.

47. The catalytic composition of claim 46, wherein the zeolite comprises one selected from the group consisting of MCM-41, ultrastabilized Y, NaY, H-ferrierite, $\text{AlPO}_4\text{-5}$, and ZSM-5.

48. The catalytic composition of claim 47, wherein the precious metal comprises one selected from the group consisting of Pt, Pd, Rh, Ru, Ir, and combinations thereof.

49. The catalytic composition of claim 47, wherein the metal oxide comprises Al_2O_3 .

50. A catalytic unit for reducing NO_x in lean exhaust gases to N_2 using a fuel as a reductant, comprising a body extruded from a zeolite which is impregnated with at least one precious metal.

5 51. The catalyst unit of claim 50, wherein the zeolite comprises one selected from the group consisting of MCM-41, ultrastabilized Y, NaY, H-ferrierite, $\text{AlPO}_4\text{-5}$, and ZSM-5.

10 52. The catalyst unit of claim 50, wherein the zeolite is loaded with a metal selected from the group consisting of Cu, Ni, In, Ga, Ag, Co, and combinations thereof.

53. The catalytic unit of claim 50, wherein the precious metal comprises one selected from the group consisting of Pt, Pd, Rh, Ru, Ir, and combinations thereof.

15 54. A catalytic unit for reducing NO_x in exhaust gases to N_2 using a fuel as a reductant, comprising a ceramic substrate coated with at least one metal oxide impregnated with at least one precious metal.

20 55. The catalytic unit of claim 54, wherein the metal oxide comprises TiO_{2-x} .

56. The catalytic unit of claim 54, wherein the precious metal comprises one selected from the group consisting of Pt, Pd, Rh, Ru, Ir, and combinations thereof.

25 57. A catalytic unit for reducing NO_x in exhaust gases to N_2 using a fuel as a reductant, comprising a ceramic substrate coated with a perovskite compound represented by the formula $\text{AB}_{1-x}\text{PM}_x\text{O}_3$, where A is a rare-earth metal, B is a transition metal, PM is a precious metal, and O is oxygen.

30 58. The catalyst unit of claim 57, wherein A comprises lanthanum, B comprises manganese, PM comprises platinum, and x ranges from about 0.01 to 0.3.

59. A catalytic unit for reducing NO_x in exhaust gases to N_2 using a fuel as a reductant, comprising a ceramic substrate coated with a combination of a zeolite and at least one metal oxide impregnated with at least one precious metal.

5 60. The catalytic unit of claim 59, wherein the zeolite comprises one selected from the group consisting of MCM-41, ultrastabilized Y, NaY, H-ferrierite, $\text{AlPO}_4\text{-5}$, and ZSM-5.

10 61. The catalytic unit of claim 59, wherein the precious metal comprises one selected from the group consisting of Pt, Pd, Rh, Ru, Ir, and combinations thereof.

62. The catalytic unit of claim 59, wherein the metal oxide comprises Al_2O_3 .

ABSTRACT

A method for reducing NO_x in lean exhaust gases to N_2 includes injecting a fuel into the exhaust gases and passing the exhaust gases and fuel mixture through a catalyst to reduce the NO_x to N_2 . The catalyst may be (a) a perovskite compound, (b) at least one metal oxide impregnated with at least one precious metal, (c) a zeolite impregnated with at least one precious metal, or (d) a combination of a zeolite and at least one metal oxide impregnated with at least one precious metal.

5

Patent Application No. 10/000,000

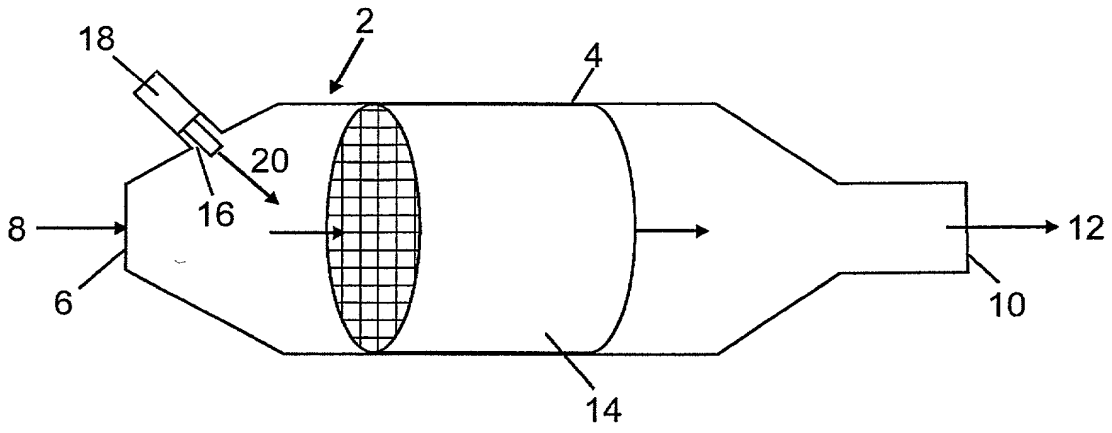


FIGURE 1

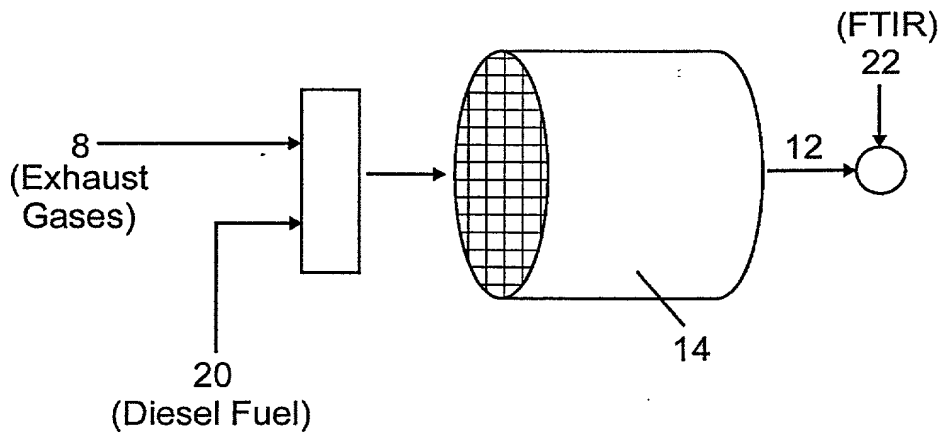


FIGURE 2

As a below named inventor, I declare that:

My residence, Post Office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled **REDUCTION OF NITROGEN OXIDES IN DIESEL EXHAUST GASES AND FUEL INJECTION SYSTEM**.

The specification of which (check only one item below):

☒ is attached hereto

☐ was filed as United States Application Serial No. on
and was amended on (if applicable)

☐ was filed as PCT international application number , on , and was
amended under PCT Article 19 on (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate or 365(a) of any PCT international application which designated at least one country other than the United States, listed below and have also identified below any foreign application for patent or inventor's certificate, on the same subject matter, having a filing date before that of the application on which priority is claimed:

<input type="checkbox"/>	Country:	Application No.:	Filing Date:
<input checked="" type="checkbox"/>	NONE		

I hereby claim the benefit under Title 35 United States Code § 119(e) and § 120 of any United States application(s) or 365(c) of any PCT international application designating the United States listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35 United States Code § 112, I acknowledge the duty to disclose material information as defined in Title 37 Code of Federal Regulations, § 1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

<input type="checkbox"/>	Provisional No.:	Filed:	Status:
<input type="checkbox"/>	Application No.:	Filed:	Status:
	PCT Application No:	Filed:	Status:
<input checked="" type="checkbox"/>	NONE		

DECLARATION IN ORIGINAL APPLICATION

U.S. Attorney Docket No.: SP00-290

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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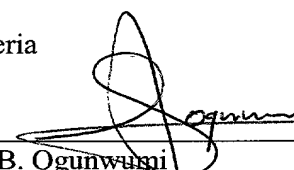
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(U.S.)

Attorney Docket No.: SP00-290

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): He, et al

Serial No.:

Filed:

For: REDUCTION OF NITROGEN OXIDES
IN DIESEL EXHAUST GASES AND
FUEL INJECTION SYSTEM

**COMBINED
CERTIFICATE UNDER
37 C.F.R. § 3.73(b)
and
POWER OF ATTORNEY**

Assistant Commissioner for Patents
Washington, DC 20231

CERTIFICATE UNDER 37 C.F.R. § 3.73(b)

CORNING INCORPORATED, a New York corporation, certifies that it is the assignee of the entire right, title and interest in the patent application identified above by virtue of an assignment from the inventor(s) of the patent application identified above. A true copy of the unrecorded Assignment is attached hereto.

The undersigned has reviewed the above referenced assignment of the patent application identified above and, to the best of the undersigned's knowledge and belief, title is in the assignee identified above.

The undersigned is empowered to sign this certificate on behalf of the assignee.

I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful false statements, and the like so made, are punishable by fine or imprisonment, or both, under Section 1001, Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

POWER OF ATTORNEY BY ASSIGNEE

CORNING INCORPORATED, the assignee of the full and exclusive right, title and interest in and to the accompanying application for United States Letters Patent entitled **REDUCTION OF NITROGEN OXIDES IN DIESEL EXHAUST GASES AND FUEL INJECTION SYSTEM** and executed by Lin He and Steven B. Ogunwumi on 10/6/00, respectively, appoints the practitioners associated with the Customer Number provided below (i.e., the practitioners associated with the Patent Department, Corning Incorporated) to prosecute this application and to transact all business in the U.S. Patent and Trademark Office connected therewith. Please direct all correspondence to Anca C. Gheorghiu at the address associated with that Customer Number.

Customer Number: 22928

CORNING INCORPORATED

Date: 10-9-00

By



Alfred L. Michaelson
Senior Vice President